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(54) **Planographic printing plate precursor**

(57) A positive planographic printing plate precursor comprising a recording layer containing a water-insoluble and alkali-soluble resin, an infrared absorbent and an organic quaternary ammonium salt. A positive planographic printing plate precursor comprising at least

two recording layers containing the resin and the infrared absorbent with a coating amount of an upper positive recording layer being in the range of 0.05 to 0.45 g/m<sup>2</sup>.

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[0008] Although various dissolution inhibitors have been proposed to improve resistance to developability, few can rapidly terminate the inhibition effect by exposure to light. In order to enhance resistance to solubility of the unexposed portions (image portions) in a developer without reducing the developability of the exposed portions (non-image portions), European Patent No. 950517 discloses a method using a siloxene type surfactant, and Japanese Patent Application Laid-Open (JP-A) No. 10-26851 discloses a method in which sulfonic esters are used as dissolution inhibitors. Such methods may improve resistance to development of the image portions of the recording layer, but do not achieve a sufficient difference in the solubilities of the unexposed portions and the exposed portions to the extent that clear and better image can be formed regardless of variance in the activity of the developer.

## 10 SUMMARY OF THE INVENTION

[0009] An object of the present invention is to provide a positive planographic printing plate precursor that is exposed to an infrared laser in direct plate formation, with the plate precursor including a recording layer that can form excellent images, has excellent sensitivity and development latitude at the time an image is formed, and with which the generation of defects resulting from scratches on image portions is suppressed.

[0010] As a result of their intensive study, the present inventors found that a planographic printing plate having excellent development latitude can be obtained by incorporating an organic quaternary ammonium salt as a dissolution inhibitor in a layer which comprises a water-insoluble and alkali-soluble resin.

[0011] The present inventors also found that a planographic printing plate precursor that has high sensitivity, with which the influence of scratches is suppressed, and that can form excellent images free from defects, can be obtained by disposing on a support at least two recording layers including a light-heat converting agent, incorporating in both the upper and lower recording layers an infrared-absorbing dye, and controlling the coating amount of the layers in a predetermined range.

[0012] A first aspect of the present invention is a positive planographic printing plate precursor. The precursor comprises a support having disposed thereon a positive recording layer containing (A) a water-insoluble and alkali-soluble resin, (B) an infrared absorbent and (C) an organic quaternary ammonium salt, wherein solubility of the recording layer in an aqueous alkali solution is increased by exposure to an infrared laser.

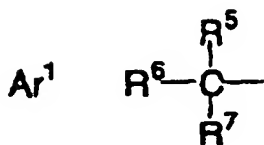
[0013] As the (C) organic quaternary ammonium salt used herein, a salt having in a molecule thereof at least one group of an aryl group and a carbonyl group is preferable from the viewpoint of effects.

[0014] Although the mechanism resulting in the action of the present invention is not entirely clear, by incorporating the (A) water-insoluble and alkali-soluble resin (hereinafter, "alkali-soluble resin") and the (C) organic quaternary ammonium salt in the same recording layer, a dry film is formed in a state that is energetically stable (i.e., a state in which there has been interaction between both compounds). Because the effect of inhibiting dissolution into an alkaline solution can be obtained at unexposed portions by this interaction, excellent resistance to alkali development in the portions is manifested in comparison with a case in which the (A) alkali-soluble resin is used by itself. Furthermore, because the (C) organic quaternary ammonium salt has a chemical structure in which the nitrogen cation is complicatedly surrounded by groups and therefore the interaction between the (A) alkali-soluble resin and the (C) organic quaternary ammonium salt is relatively small, the interaction is effectively terminated (released) at regions where the (B) infrared absorbent has generated heat due to exposure to the infrared laser. In addition, since the (C) organic quaternary ammonium salt itself is a low-molecular compound, it is easily dispersed in an aqueous alkaline solution when the interaction has been terminated, and dissolution-accelerating properties can be obtained. For these reasons, it is surmised that using the (C) organic quaternary ammonium salt results in a large difference in the solubilities in an alkali developer of the unexposed portions and the exposed portions, whereby it is possible to obtain a better image regardless of variations of the concentration of the developer.

[0015] A second aspect of the present invention is a positive planographic printing plate precursor. The precursor comprises a support having disposed thereon at least two positive recording layers containing a water-insoluble and an alkali-soluble resin and an infrared-absorbing dye, with solubility of the recording layer in an aqueous alkali solution being increased by exposure to an infrared laser, wherein a coating amount of an upper positive recording layer is in the range of 0.05 to 0.45 g/m<sup>2</sup>.

[0016] The positive recording layer having a coating amount in the range of 0.05 to 0.45 g/m<sup>2</sup> is preferably located nearest to the surface among a plurality of positive recording layers. For example, when two positive recording layers are disposed on the support, the upper positive recording layer is the one having a coating amount in the range of 0.05 to 0.45 g/m<sup>2</sup>, and when three positive recording layers are disposed on the support, the uppermost positive recording layer is the one having a coating amount in the range of 0.05 to 0.45 g/m<sup>2</sup>. The positive recording layer closest to the surface is referred to below as the upper(most) recording layer.

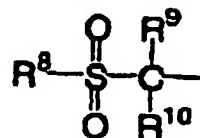
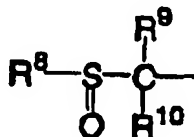
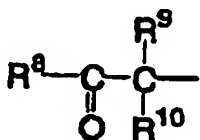
[0017] It is not entirely clear why sensitivity, development latitude and resistance of image portions to scratches are excellent in the positive planographic printing plate precursor of the second aspect. It is surmised that by coating on a support at least two positive recording layers including an infrared-absorbing dye, with the coating amount of the



In the units, Ar<sup>1</sup> represents an aryl group, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> represent independently a hydrogen atom or an organic group having one or more carbon atoms, at least two of R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are not a hydrogen atom, and R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> may be bonded with each other to form a ring.

[0023] Another suitable examples of the organic quaternary ammonium salt compound represented by the general formula (I) include a compound wherein at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is selected from the group consisting of functional groups (structures) shown below (referred to a group A).

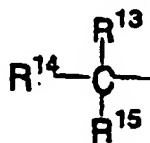
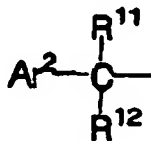
#### Group A



In the formulas, R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> represent independently a hydrogen atom or an organic group having one or more carbon atoms, at least two of R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> are selected from an organic group which is not a hydrogen atom, that is, these are not a hydrogen atom, and R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> may be bonded with each other to form a ring.

[0024] More preferable examples of the organic quaternary ammonium salt compounds represented by the general formula (I) include a compound wherein at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is selected from the group consisting of functional groups (structures) shown below (referred to a group B).

#### Group B

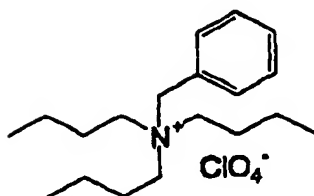


In the formulas, Ar<sup>2</sup> represents an aryl group, R<sup>11</sup> and R<sup>12</sup> represent independently a hydrogen atom or an organic group having one or more carbon atoms, and Ar<sup>2</sup>, R<sup>11</sup> and R<sup>12</sup> may be bonded with each other to form a ring. R<sup>13</sup>, R<sup>14</sup> and R<sup>15</sup> represent independently a hydrogen atom or an organic group having one or more carbon atoms, and at least one of R<sup>13</sup>, R<sup>14</sup> and R<sup>15</sup> is a non-aromatic cyclic substituent, or adjacent two groups of R<sup>13</sup>, R<sup>14</sup> and R<sup>15</sup> may be bonded with each other to form a ring.

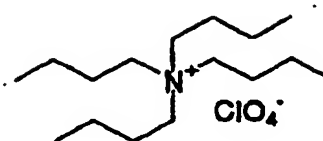
[0025] Most preferable examples of the organic quaternary ammonium salt compound represented by the general formula (I) include a compound wherein R<sup>8</sup> in the functional groups of the group A is an aryl group and a compound wherein at least two of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are selected from the groups A and B. Among them, a compound which comprises at least one group selected from the group A and at least one group selected from the group B is most preferable.

[0026] Concrete examples of the preferable organic quaternary ammonium salt which can be used in the present

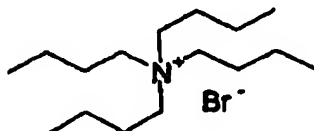
Ammonium salt (7)



Ammonium salt (8)



Ammonium salt (9)



Ammonium salt (10)



[0027] It is preferable that the (C) organic quaternary ammonium salt is contained at 0.1 to 40% by weight, preferably 0.5 to 10% by weight of the total solid component of the positive recording layer. When the content of the (C) organic quaternary ammonium salt is too small such that the (C) organic quaternary ammonium salt is contained in an amount of less than 0.1 % by weight, it is difficult to obtain the effects of the present invention. When the content is too large, the content of an alkali-soluble resin to be used in combination with the (C) organic quaternary ammonium salt is relatively reduced and, thus, there is a possibility that abrasion resistance during printing is lowered.

#### [(A) Water-insoluble and alkali-soluble resin]

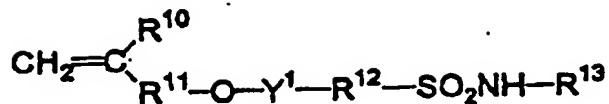
[0028] The water-insoluble and alkali-soluble resin used in the present invention is not particularly limited as long as it has been already known and utilized. However, a polymer compound having in a molecule at least one of (1) a phenolic hydroxy group, (2) a sulfonamide group and (3) an active imide group is preferable as the resin. As concrete examples of the alkali-soluble polymer, which can be suitably used in the present invention, examples are shown below, however, they are not intended to limit the alkali-soluble polymers.

#### (1) Resin having a phenolic hydroxyl group

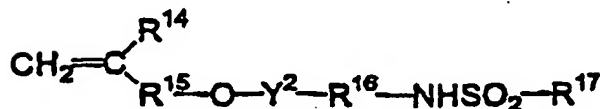
[0029] Examples of the resin having a phenolic hydroxyl group include novolac resins such as phenol/formaldehyde resins, m-cresol/formaldehyde resins, p-cresol/formaldehyde resins, m-cresol/p-cresol/formaldehyde resins, 2,5-xyleneol/formaldehyde resins, 3,5-xyleneol/formaldehyde resins, phenol/cresol (this cresol may be m-cresol, p-cresol or a mixture of m-cresol and p-cresol) formaldehyde resins, phenol/xyleneol formaldehyde resins, xyleneol/cresol (this cresol may be m-cresol, p-cresol or a mixture of m-cresol and p-cresol) formaldehyde resins and phenol/cresol/xyleneol formaldehyde resins, and pyrogallol/acetone resins.

[0030] Further, resins described in U.S. Pat. No. 4,123,279 wherein resins such as t-butylphenol formaldehyde resin and octylphenol formaldehyde resin are obtained by a condensation polymerization reaction between a formaldehyde and a phenol having as a substituent an alkyl group containing 3 to 8 carbon atoms, can be used.

[0031] Preferable examples of the polymer compound having a phenolic hydroxyl group include a polymer compound having at least one of phenolic hydroxyl group on a side chain thereof. Examples of the polymer compound having at least one of phenolic hydroxyl group on a side chain include a polymer compound which is obtained by monopolymerization of a polymerizable monomer of a low-molecular compound having one or more phenolic hydroxyl groups and



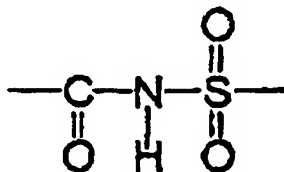
General formula (d)



General formula (e)

In the formulas,  $\text{X}_1$  and  $\text{X}_2$  each represent -O- or -NR<sub>7</sub>-, R<sup>1</sup> and R<sup>4</sup> each represent a hydrogen atom or -CH<sub>3</sub>. R<sup>2</sup>, R<sup>5</sup>, R<sup>9</sup>, R<sup>12</sup> and R<sup>16</sup> each represent an alkylene group having 1 to 12 carbon atoms, a cycloalkylene group, an arylene group or an aralkylene group, each optionally may be substituted. R<sup>3</sup>, R<sup>7</sup> and R<sup>13</sup> represent a hydrogen atom, an alkyl group having 1 to 12 carbon atoms, a cycloalkyl group, an aryl group or an aralkyl group, each optionally may be substituted. R<sup>6</sup> and R<sup>17</sup> represent an alkyl group having 1 to 12 carbon atoms, a cycloalkyl group, an aryl group or an aralkyl group, each optionally may be substituted. R<sup>8</sup>, R<sup>10</sup> and R<sup>14</sup> represent a hydrogen atom or -CH<sub>3</sub>. R<sup>11</sup> and R<sup>15</sup> each represent a single bond or an alkylene group having 1 to 12 carbon atoms, a cycloalkylene group, an arylene group or an aralkylene group, each optionally may have a substituent. Y<sup>1</sup> and Y<sup>2</sup> each represent a single bond or -CO-. Concrete examples of the compound include m-aminosulfonylphenyl methacrylate, N-(p-aminosulfonylphenyl)methacrylamide and N-(p-aminosulfonylphenyl)acrylamide which can be appropriately used.

[0035] (3) Alkali-soluble resin having an active imide group An alkali-soluble resin having an active imide group has in a molecule preferably an active imide group represented by the following formula. Examples of this polymer compound include polymer compounds obtained by polymerization of a polymerizable monomer of a low-molecular compound having in a molecule one or more active imide groups represented by the following formula and one or more polymerizable unsaturated bonds, or by copolymerization of the polymerizable monomer with another polymerizable monomer.



[0036] Concrete examples of the compound include N-(p-toluenesulfonyl)methacrylamide, N-(p-toluenesulfonyl)acrylamide.

[0037] As the alkali-soluble resin of the present invention, a rovolac resin is preferable.

[0038] Preferable examples of the alkali-soluble resin also include polymer compounds obtained by polymerization of two or more polymerizable monomers selected from the group consisting of the polymerizable monomer having a phenolic hydroxyl group, the polymerizable monomer having a sulfonamide group and the polymerizable monomer having an active imide group, and polymer compounds obtained by copolymerization of two or more polymerizable monomers and another polymerizable monomer. When the polymerizable monomer having a phenolic hydroxyl group is copolymerized with the polymerizable monomer having a sulfonamide group and/or the polymerizable monomer having an active imide group, the blending weight ratio thereof is in the range of from 50:50 to 5:95, and preferably in the range of from 40:60 to 10:90.

[0039] When the alkali-soluble resin of the present invention is a polymer compound which is obtained by copolymerization of another polymerizable monomer and at least one monomer selected from the group consisting of the polymerizable monomer having a phenolic hydroxyl group, the polymerizable monomer having a sulfonamide group

pigments, nitroso pigments, nitro pigments, natural pigments, fluorescent pigments, inorganic pigments, and carbon black.

[0046] These pigments may be used without being surface-treated or may be used after being surface-treated. Possible surface treatments include a treatment in which a resin or a wax is coated on the surface of the pigments, a treatment in which a surfactant is adhered to the surface of the pigment, and a treatment in which a reactive substance (e.g., a silane coupling agent, an epoxy compound or a polyisocyanate) is bonded to the surface of the pigment. These surface-treating methods are described in "Properties and Applications of Metal Soaps" (Saiwai Shobo Co., Ltd.), "Printing Ink Technologies" (Insatsu Inki Gijutsu), CMC, 1984 and "Latest Pigment Application Technologies" (Saishin Ganryo Oyo Gijutsu), CMC, 1986.

[0047] The diameter of the pigments is preferably 0.01  $\mu\text{m}$  to 10  $\mu\text{m}$ , more preferably 0.05  $\mu\text{m}$  to 1  $\mu\text{m}$ , and most preferably 0.1  $\mu\text{m}$  to 1  $\mu\text{m}$ . If the diameter is less than 0.01  $\mu\text{m}$ , the dispersion stability of the pigments in a coating liquid to form a photosensitive layer is insufficient, whereas, if the diameter is greater than 10  $\mu\text{m}$ , the uniformity of the photosensitive layer after coating thereof is poor. A known dispersing technology using a dispersing machine employed in the preparation of ink and toners can also be used for the purpose of dispersing the pigments. Examples of the dispersing machine include an ultrasonic wave dispersing machine, a sand mill, an attritor, a pearl mill, a super mill, a ball mill, an impeller, a disperser, a KD mill, a colloid mill, a dynatron, a three-roller mill, and a pressurized kneader. Details of these dispersing technologies are described in "Latest Pigment Application Technologies" (Saishin Ganryo Oyo Gijutsu), CMC, 1986.

[0048] The dyes suitable for use in the present invention are commercially available dyes and those described in, for example, "Handbook of Dyes" edited by Association of Organic Synthesis (Yuki Gosei Kagaku Kyokai) (1970). Concrete examples of the dyes include azo dyes, azo dyes in the form of a metallic complex salt, pyrazolone azo dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinonimine dyes, methine dyes, and cyanine dyes. Among these pigments and dyes, the pigments or dyes which absorb infrared light or near-infrared light are particularly preferable in the present invention, because they are suitable to use in a laser emitting infrared light or near-infrared light.

[0049] A suitable pigments which absorbs infrared light or near-infrared light is carbon black. Concrete examples of dyes which absorb infrared light or near-infrared light include cyanine dyes described in, e.g., Japanese Patent Application Laid-Open (JP-A) Nos. 58-125246, 59-84356, 59-202829, and 60-78787, methine dyes described in, e.g., JP-A Nos. 58-173696, 58-181690, and 58-194595, naphthoquinone dyes described in, e.g., JP-A Nos. 58-112793, 58-224793, 59-48187, 59-73996, 60-52940 and 63-62744, squarylium dyes described in JP-A No. 58-112792 and cyanine dyes described in U.K. Patent No. 434,875.

[0050] Another suitable dye is the near-infrared absorbing sensitizer described in U.S. Pat. No. 5,156,938, and a substituted arylbenzo (thio) pyrylium salt described in U.S. Pat. No. 3,881,924, a trimethine thiapyrylium salt described in JP-A No. 57-142645 (U.S. Pat. No. 4,327,169), pyrylium-based compounds described in JP-A Nos. 58-181051, 58-220143, 59-41363, 59-84248, 59-84249, 59-146063 and 59-146061, a cyanine dye described in JP-A No. 59-216146, a pentamethine thiopyrylium salt described in U.S. Pat. No. 4,283,475, and pyrylium-based compounds described in Japanese Patent Application Publication (JP-B) Nos. 5-13514 and 5-19702, Epolight III-178, Epolight III-130, Epolight III-125 and the like manufactured by manufactured by Epolin Co., Ltd. are most preferably used.

[0051] Further examples of the preferred dyes are near-infrared-absorbing dyes represented by the formulas (I) and (II) in U.S. Pat. No. 4,756,993. The amounts of the dye and the pigment are each in the range of from 0.01 to 50% by weight and preferably in the range of from 0.1 to 10% by weight based on the total solid component of the material for a printing plate. Most preferably, the amount of the dye is in the range of from 0.5 to 10% by weight, while the amount added of the pigment is in the range of from 3.1 to 10% by weight based on the weight of the total solids of the material for a printing plate. If the amount of the pigment or the dye is less than 0.01% by weight, the sensitivity of the material for a printing plate may decrease, whereas, if the amount added is more than 50% by weight, the photosensitive layer becomes nonuniform and the durability of the recording layer is poor. The dye or the pigments may be added to the same layer together with other components, or otherwise the dye or the pigment may be added to a separate layer provided additionally. If the dye or the pigment is added to a separate layer, it is desirable that the layer to which the dye or the pigment is added is a layer adjacent to the layer containing a substance which is thermally degradable but capable of substantially decreasing the solubility of a binder when in an undegraded state. The dye or the pigment is added preferably to a layer containing a binder resin, but may be added to a separate layer.

[Other components]

[0052] According to needs, a variety of additives may be incorporated into the positive photosensitive composition of the present invention. For example, from the standpoint of more effective inhibition of the dissolution of the image areas into a developing solution, it is desirable to incorporate a substance, such as an onium salt, an o-quinone diazide compound, an aromatic sulfone compound, or an aromatic sulfonate compound. These substances are thermally de-

hydride, hexahydrophthalic anhydride, 3,6-endoxy-A4-tetrahydrophthalic anhydride, tetrachlorophthalic anhydride, maleic anhydride, chloromaleic anhydride,  $\alpha$ -phenylmaleic anhydride, succinic anhydride, and pyromellitic anhydride as described in U.S. Pat. No. 4,115, 128. Examples of the phenol include bisphenol A, p-nitrophenol, p-ethoxyphenol, 2,4,4'-trihydroxybenzophenone, 2,3,4-trihydroxybenzophenone, 4-hydroxybenzophenone, 4,4',4"-trihydroxytriphenylmethane and 4,4',3",4"-tetrahydroxy-3,5,3',5'-tetramethyltriphenylmethane. Examples of the organic acid include sulfonic acids, sulfinic acids, alkylsulfuric acids, phosphonic acids, phosphates, and carboxylic acids as described in, e. g., JP-A Nos. 60-88942 and 2-96755. Concrete examples of these organic acids include p-toluenesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfinic acid, ethylsulfuric acid, phenylphosphonic acid, phenylphosphinic acid, phenyl phosphate, diphenyl phosphate, benzoic acid, isophthalic acid, adipic acid, p-toluic acid, 3,4-dimethoxybenzoic acid, phthalic acid, terephthalic acid, 4-cyclohexene-1,2-dicarboxylic acid, erucic acid, lauric acid, n-undecanoic acid, and ascorbic acid. The amount added of the cyclic acid anhydride, the phenol, and the organic acid is in the range of from 0.05 to 20% by weight, more preferably in the range of from 0.1 to 15% by weight, and most preferably in the range of from 0.1 to 10% by weight based on the weight of the total solids of the material for a printing plate.

[0061] Further, in order to broaden the stable range of processing conditions, the coating solution for the printing plate of the present invention may be contained a nonionic surfactant as described in JP-A Nos. 62-251740 and 3-208514, an amphoteric surfactant as described in JP-A Nos. 59-121044 and 4-13149, siloxane based compound as described in EP 950517, and a copolymer of a fluorine containing monomer as described in JP-A No. 11-288093.

[0062] Concrete examples of the nonionic surfactant include sorbitan tristearate, sorbitan monopalmitate, sorbitan trioleate, stearic acid monoglyceride, and polyoxyethylene nonylphenyl ether. Concrete examples of the amphoteric surfactant include alkyldi(aminoethyl)glycine, hydrochloric acid salt of alkylpolyaminoethylglycine, 2-alkyl-N-carboxyethyl-N-hydroxyethylimidazolinium betaine, and N-tetradecyl-N, N-betaine (e.g., Amogen K manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.).

[0063] As a siloxane compound, a block copolymer of dimethylsiloxane and polyalkylene oxide is preferable and embodiments thereof include polyalkylene oxide-modified silicones such as DBE-224, DBE-621, DBE-712, DBE-732 and DBE-534 manufactured by Chisso K.K. and Tego Glide100 and the like manufactured by Tego Company in Germany.

[0064] The preferred amounts added of the nonionic surfactant and the amphoteric surfactant are each in the range of from 0.05 to 15% by weight, more preferably from 0.1 to 5% by weight, based on the total solids weight of the material for a printing plate.

[0065] In the present invention, the material for a printing plate may contain a dye or a pigment as a printing-out agent which makes it possible to produce a visible image immediately after heating caused by exposure and also as an image coloring agent.

[0066] A typical example of the printing-out agent is a combination of a compound, which releases an acid by heating caused by exposure (i.e., a photoacid releasing agent) and an organic dye capable of forming a salt with the foregoing compound. Concrete examples of the printing-out agent include a combination of o-naphthoquinonediazide-4-sulfonyl halogenide and an organic dye which forms a salt with this compound as described in JP-A Nos. 50-36209 and 53-8128 as well as a combination of a trihalomethyl compound and an organic dye which forms a salt with this compound as described in JP-A Nos. 53-36223, 54-74728, 60-3626, 61-143748, 61-151644, and 63-58440. Examples of the trihalomethyl compound are an oxazole-based compound and a triazine-based compound, both of which are effective in providing a good storability and a clear printed out image.

[0067] A dye other than the above-mentioned salt-forming organic dyes can also be used as an image coloring agent. Examples of suitable dyes include oil-soluble dyes and basic dyes in addition to the salt-forming organic dyes. Specific examples of these dyes include Oil Yellow No. 101, Oil Yellow No. 103, Oil Pink No. 312, Oil Green BG, Oil Blue BOS, Oil Blue No. 603, Oil Black BY, Oil Black BS, and Oil Black T-505 (all manufactured by Orient Chemical Industries, Co., Ltd.), Victoria Pure Blue, Crystal Violet (C.I. 42555), Methyl Violet (C.I. 42535), Ethyl Violet, Rhodamine B (C.I. 145170B), Malachite Green (C.I. 42000), and Methylene Blue (C.I. 52015). The dyes described in JP-A No. 62-293247 are particularly preferable. The amount added of the dye is in the range of from 0.01 to 10% by weight and more preferably in the range of from 0.1% to 3% by weight based on the weight of the total solid materials for a printing plate. In order to impart flexibility to the layer, a plasticizer is incorporated into the material for a printing plate of the present invention. Examples of the plasticizer include butyl phthalate, polyethylene glycol, tributyl citrate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, dioctyl phthalate, tricresyl phosphate, tributyl phosphate, trioctyl phosphate, tetrahydrofurfuryl oleate, and an oligomer or a polymer of acrylic acid or methacrylic acid.

[0068] The image recording layer of the present invention is usually formed by coating a coating liquid, which is prepared by dissolving the above-described components in a solvent, on an appropriate support.

[0069] Some illustrative nonlimiting examples of the solvent include ethylene dichloride, cyclohexanone, methyl ethyl ketone, methanol, ethanol, propanol, ethylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, N,N-dimethylacetamide, N,N-dimethylformamide, tetramethylurea, N-methylpyrrolidone, dimethyl sulfoxide, sulfolane,  $\gamma$ -butyrolactone, and toluene. These

deposited with aluminum. Examples of the other elements which may be contained in the aluminum alloy include silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel, and titanium. The total content of the other elements in the aluminum alloy is 10% by weight or less. Although the aluminum particularly desirable for use in the present invention is pure aluminum, the aluminum to be used in the present invention may contain a small amount of other elements, because limitations in purification technologies make the production of perfectly pure aluminum difficult.

[0081] Accordingly, the composition of the aluminum plate for use in the present invention is not particularly limited, and a conventionally known aluminum plate as a material may be used appropriately in the present invention. The thickness of the aluminum plate for use in the present invention is about 0.1 mm to 0.6 mm, preferably 0.15 mm to 0.4 mm, and most preferably 0.2 mm to 0.3 mm.

[0082] Prior to the surface-roughening of the aluminum plate, if necessary, a degreasing treatment is performed in order to remove any rolling oil from the surface of the aluminum plate by means of a surfactant, an organic solvent, an aqueous alkaline solution, or the like. The surface-roughening of the aluminum plate may be performed by a variety of methods. Examples of these methods include a method in which the surface is mechanically roughened, a method in which the surface is roughened by being electrochemically dissolved, and a method in which the surface is selectively dissolved in a chemical way. The mechanical methods may be conventionally known methods such as ball abrasion, brushing, blasting and buffing. Examples of the electrochemical methods include electrolysis of the aluminum plate in an electrolyte solution, such as a hydrochloric acid or a nitric acid, using an AC current or a DC current. A combination of a mechanical method and an electrochemical method is also possible as described in JP-A No. 54-63902. If necessary, the surface-roughened aluminum plate is then subjected to an alkali-etching treatment and a neutralizing treatment. After that, if desired, the aluminum plate is subjected to an anodizing treatment so as to increase the water retention and wear resistance of the surface. A variety of electrolytes capable of producing a porous oxide layer can be used as an electrolyte for the anodizing treatment of the aluminum plate. Generally, sulfuric acid, phosphoric acid, oxalic acid, chromic acid, or a mixture of those acids is used as the electrolyte. The concentration of the electrolyte may be determined appropriately depending on the type of the electrolyte.

[0083] Conditions for the anodizing vary depending on the types of electrolyte solutions employed and cannot be stipulated unqualifiedly. However, generally employed conditions are as follows: concentration of the electrolyte solution is 1 to 80% by weight; temperature of the solution is 5 to 70°C; current density is 5 to 60 A/dm<sup>2</sup>; voltage is 1 to 10V; and duration of the electrolysis is 10 seconds to 5 minutes. If the amount of the anodized layer is less than 1.0 g/m<sup>2</sup>, the surface has poor printing durability and therefore the non-image areas of a resulting planographic printing plate are liable to form scratch marks, which collect printing ink in printing to produce so-called scratch smudge. If necessary, the aluminum support whose surface is anodized may be rendered hydrophilic by a surface treatment. Examples of this hydrophilic treatment used in the present invention include treating the surface with an aqueous solution of an alkali metal silicate (such as sodium silicate) as described in U.S. Pat. Nos. 2,714,066, 3,181,461; 3,280,734, and 3,902,734, in which the support is simply immersed or electrolytically treated in an aqueous solution of sodium silicate. Further examples are a treatment of the surface with an aqueous solution of potassium fluorozirconate as described in Japanese Patent Application Publication (JP-B) No. 36-22063 and a treatment of the surface with an aqueous solution of polyvinylsulfonic acid as described in U.S. Pat. Nos. 3,276,868, 4,153,461 and 4,689,272.

[0084] If necessary, a subbing layer may be formed between the foregoing layer and the support.

[0085] Various organic compounds may be used as components for the subbing layer. For example, an organic compound constituting the subbing layer is selected from the group consisting of carboxymethyl cellulose, dextrin, gum arabic, phosphonic acids having an amino group such as 2-aminoethylphosphonic acid, organic phosphonic acids which may have a substituent such as phenylphosphonic acid, naphthylphosphonic acid, alkylphosphonic acid, glycerophosphonic acid, methylenediphosphonic acid, and ethylenediphosphonic acid, organic phosphoric acids which may have a substituent such as phenylphosphoric acid, naphthylphosphoric acid, alkylphosphoric acid, and glycerophosphoric acid, organic phosphinic acids which may have a substituent such as phenylphosphinic acid, naphthylphosphinic acid, alkylphosphinic acid, and glycerophosphinic acid, amino acids such as glycine and  $\beta$ -alanine, and hydrochloric acid salts of amines having a hydroxyl group such as hydrochloric acid salt of triethanolamine. These compounds may be used singly or may be used in a combination of two or more.

[0086] The organic subbing layer may be formed by any method described below. For example, the above-mentioned organic compound is dissolved in water, an organic solvent such as methanol, ethanol or methyl ethyl ketone, or a mixture thereof to prepare a coating solution, and thereafter, the coating solution is applied to an aluminum plate to provide a subbing layer which is then dried. Alternatively, the above-mentioned organic compound is dissolved in water, an organic solvent such as methanol, ethanol or methyl ethyl ketone, or a mixture thereof to prepare a coating solution, and thereafter an aluminum plate is immersed in the coating solution so that the organic compound is adsorbed on the surface of the aluminum plate to form a subbing layer which is then water-rinsed and dried. When the former method is employed, a solution containing 0.005 to 10% by weight of the organic compound can be applied by a variety of methods. When the latter method is employed, the parameters of the conditions are as follows: concentration of the



that an aluminum plate and the like widely used as a support for a planographic printing plate precursor are etched. When it exceeds 3.0, the developability may be reduced.

[0100] In addition, the concentration of silicate alkali in a developing solution is preferably 1 to 10% by weight, more preferably 3 to 8% by weight, most preferably 4 to 7% by weight relative to the weight of an aqueous alkali solution.

[0101] When the concentration is less than 1% by weight, the developability and the processing ability may be reduced. When it exceeds 10% by weight, the precipitates and crystals are easily produced and, further, a gel is easily formed upon neutralization at solution waste, leading to disorder of solution waste treatment.

[0102] Then, "a non-silicate developing solution" will be explained. This developing solution comprises a non-reducing sugar and a base as described above. Herein, a non-reducing sugar means sugars which have no reducing properties because they have no free aldehyde group or ketone group. The non-reducing sugars are classified into trehalose-type oligosaccharides in which reducing groups are bound each other, glycosides in which a reducing group of sugars and non-sugars are bound, and sugar alcohols obtained by reducing sugars by addition of hydrogen. In the present invention, any of them can be used appropriately.

[0103] Examples of the trehalose-type oligosaccharide include saccharose and trehalose. Examples of the glycoside include alkyl glycoside, phenol glycoside, mustard oil glycoside and the like.

[0104] Examples of the sugar alcohol include D,L-arabitol, ribitol, xylitol, D,L-sorbitol, D,L-annitol, D,L-iditol, D,L-talitol, zulcitol, allosulcitol and the like.

[0105] Further, maltitol obtained by hydrogenating disaccharides, reduced substances obtained by hydrogenating oligosaccharide (reduced millet jelly) and the like may be exemplified.

[0106] Among them, as a non-reducing sugar, sugar alcohol and saccharose are preferable. Inter alia, D-sorbitol, saccharose and reduced millet jelly are more preferable because they provide a buffer action at a suitable pH area.

[0107] These non-reducing sugars may be used singly or in combinations of two or more. The proportion of the non-reducing sugar in a developing solution is preferably 0.1 to 30% by weight, more preferably 1 to 20% by weight.

[0108] An alkaline material as a base may be appropriately selected from previously known ones and may be combined with silicic alkali or non-reducing sugar.

[0109] Examples of the alkaline substance include an inorganic alkaline substance such as sodium silicate, potassium silicate, sodium tertiary phosphate, potassium tertiary phosphate, ammonium tertiary phosphate, sodium secondary phosphate, potassium secondary phosphate, ammonium secondary phosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, ammonium hydrogencarbonate, sodium borate and potassium borate, ammonium borate, and potassium citrate, potassium tertiary citrate, sodium and sodium citrate.

[0110] In addition, an organic alkaline substance can also be used as the alkaline substance. Examples of the organic alkaline substance include monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethylenediamine, and pyridine.

[0111] These alkaline substances are used singly or in a combination of two or more.

[0112] Among them, sodium hydroxide and potassium hydroxide are preferable because pH adjustment can be performed in the wide pH region by adjusting an amount to be added to a non-reducing sugar.

[0113] In addition, sodium tertiary phosphate, potassium tertiary phosphate, sodium carbonate, potassium carbonate and the like are preferable because they themselves have the buffering activity.

[0114] In an automated developing machine, a conventionally employed replenishing system is known to be able to process a large amount of pre-sensitized plates without exchanging the developing solution in the tank for a long period of time by feeding the tank with an aqueous solution (a replenisher solution) having an alkali strength higher than that of the developing solution in the tank. This replenishing system is also suitable for use in the present invention. If necessary, the developing solution and the replenisher solution may contain a surfactant or an organic solvent for such purposes as increasing or decreasing developability, dispersing the sludge resulting from development, and increasing the hydrophilicity of the image areas of a printing plate.

[0115] Examples of preferred surfactants include anionic surfactants, cationic surfactants, nonionic surfactants, and amphoteric surfactants. Further, if necessary, the developing solution and the replenisher solution may contain a reducing agent such as hydroquinone, resorcinol, and a salt of inorganic acid, e.g., sodium or potassium sulfite and sodium or potassium hydrogensulfite, an organic carboxylic acid, a defoaming agent and an agent to convert hard water into soft water.

[0116] The printing plate after being processed with the developing solution and the replenisher solution described above is then subjected to a post-treatment such as a treatment with rinsing water containing a surfactant or the like, or a treatment with a desensitizing solution containing gum arabic or a starch derivative. A combination of these treatments may be employed as a post-treatment when the image recording material of the present invention is used as a printing plate.

[0117] Recently, for the purpose of rationalization and standardization of plate making operations, automated devel-

[0127] The upper recording layer contains a water-insoluble and alkali-soluble resin and an infrared-absorbing dye.

[0128] As the infrared-absorbing dye contained in the upper recording layer, any known infrared-absorbing dyes can be selected and used, as long as they absorb infrared-ray such as a ray of an infrared laser, and produce the heat. However, from a viewpoint of unpreferable block of exposure to the lower recording layer, a pigment which does not have light transmittance such as carbon black is not preferable, and a dye having the high infrared transmittance is preferable. Examples of the preferable infrared-absorbing dyes include an indoaniline dye, a cyanine dye, a merocyanine dye, an oxonol dye, a porphyrin derivative, an anthraquinone dye, a merostyryl dye, a pyrylium compound, a diphenyl and triphenyl azo compound, a squarylium derivative and the like.

[0129] These dyes can be added to the upper recording layer in an amount of 0.01 to 50% by weight, preferably 0.5 to 30% by weight, particularly 1 to 20% by weight based on all solids components of the upper recording layer. When an amount of a dye to be added is less than 0.1% by weight, the sensitivity is lowered, while when the amount exceeds 50% by weight, the uniformity of the recording layer is lost, the durability is lowered and, at the same time, the transmittance of an exposure to the lower recording layer is lowered and the sensitivity is lowered.

[0130] In the second aspect of the present invention, the (A) water-insoluble and alkali-soluble resin described in the first aspect can be used as the water-insoluble and alkali-soluble polymer compound (hereinafter, conveniently, referred to as alkali-soluble polymer) which is used in the recording layer of the second aspect. Further, the homopolymer containing an acidic group on a main chain and/or a side chain in a polymer, the copolymer thereof and the mixture thereof of the first aspect are also used. Therefore, a polymer layer of the second aspect of the present invention has the properties that it is dissolved when it is contacted with an alkaline developing solution.

[0131] Among them, those having an acidic group shown in the following (1) to (6) on a main chain and/or a side chain in a polymer are preferable from a viewpoint of the solubility in an alkaline developing solution.

(1) Phenolic hydroxy group (-Ar-OH)

(2) Sulfonamide group (-SO<sub>2</sub>NH-R)

(3) Substituted sulfonamide type acid group (hereinafter, referred to as "active imide group") (-SO<sub>2</sub>NHCOR, -SO<sub>2</sub>NHSO<sub>2</sub>R, -CONHSO<sub>2</sub>R)

(4) Carboxylic group (-CO<sub>2</sub>H)

(5) Sulfonic group (-SO<sub>3</sub>H)

(6) Phosphoric group (-OPO<sub>3</sub>H<sub>2</sub>)

[0132] In the acidic groups of (1) to (6), Ar represents a divalent aryl linking group optionally having a substituent, and R represents a hydrocarbon group optionally having a substituent.

[0133] Among alkali-soluble polymers having an acidic group selected from the (1) to (6), alkali-soluble polymers having (1) a phenolic hydroxy group, (2) a sulfonamide group and (3) an active imide group are preferable. In particular, alkali-soluble polymers having (1) a phenolic hydroxy group or (2) a sulfonamide group are most preferable from the viewpoint of sufficient solubility in an alkaline developing solution and film strength.

[0134] Next, a representative example of a polymerizable component for the alkali-soluble polymer compound will be described.

(1) Polymerizable monomer having a phenolic hydroxy group

[0135] Examples of a polymerizable monomer having a phenolic hydroxy group include polymerizable monomers which is a low-molecular compound having one or more of phenolic hydroxy groups and one or more polymerizable unsaturated bonds, such as acrylamide, methacrylamide, acrylic ester, methacrylic ester and hydroxystyrene.

[0136] More particularly, examples thereof include polymerizable monomers having a phenolic hydroxy group described in the first aspect of the present invention.

(2) Polymerizable monomer having a sulfonamide group

[0137] Examples of a polymerizable monomer having a sulfonamide group include polymerizable monomers which is a low-molecular compound having in one molecule one or more of sulfonamide groups (-NH-SO<sub>2</sub>-) in which at least one hydrogen atom is bound to a nitrogen atom, and one or more polymerizable unsaturated bonds. Examples thereof include low-molecular compounds having an acryloyl group, an allyl group or a vinyloxy group, and a substituted or mono-substituted aminosulfonyl group or a substituted sulfonylimino group. Such the compounds include, for example, compounds represented by the general formulas (I) to (V) described in JP-A 8-123029.

[0138] Concrete examples of the polymerizable monomer having a sulfonamide group include m-aminosulfonylphenyl methacrylate, N-(p-aminosulfonylphenyl)methacrylamide, N-(p-aminosulfonylphenyl)acrylamide and the like. The polymerizable monomers having a sulfonamide group described in the first aspect are also utilized.

near to a support will be explained below.

[0153] The lower recording layer contains a water-insoluble and alkali-soluble resin and an infrared-absorbing dye. As the water-insoluble and alkali-soluble resin contained in the lower recording layer, the same resins as those described above for the upper recording layer can be used. When an upper recording layer and a lower recording layer are provided adjacent to each other, the effects of the present invention may be decreased due to unclear boundary caused by mix or blend at a boundary portion between an upper recording layer and a lower recording layer. Therefore, in order to suppress the decrease of the effects, it is preferable that an alkali-soluble polymer used in the lower recording layer and an alkali-soluble polymer used in the upper recording layer are each having different solubility in a coating solvent. It is preferable that the lower recording layer is not dissolved in a coating solution of the upper recording layer. That is, a water-insoluble and alkali-soluble resin used in a lower recording layer and a water-insoluble and alkali-soluble resin used in an upper recording layer can have different solubilities in a coating solvent.

[0154] The alkali-soluble polymer compound may be used singly or in combination of two or more. The total content of the polymer compounds is preferably 1 to 90% by weight, more preferably 2 to 70% by weight, more preferably 2 to 50% by weight of the total solid component of the lower recording layer as in the upper recording layer.

[0155] In the second aspect of the present invention, an infrared-absorbing dye used in the lower recording layer is not particularly limited as long as it is a substance, which produces the heat by absorbing infrared light. In addition to infrared-absorbing dyes exemplified as suitable for the upper recording layer, other infrared-absorbing dyes can be used. Also in the lower recording layer, a pigment such as carbon black is not preferable from a viewpoint of coating properties. It is preferable to use an infrared-absorbing dye as a material having the light-heat converting function.

[0156] As a dye used in the layer, substances exemplified as a dye in the first aspect can be also used and preferable.

[0157] An amount of these dyes to be added is preferably in an amount of 0.01 to 50% by weight, more preferably 0.1 to 30% by weight, more 0.5 to 20% by weight, of total solid components in the lower recording layer.

[0158] When an amount of a dye to be added is less than 0.01% by weight, the sensitivity is lowered. On the other hand, when the amount exceeds 50% by weight, the uniformity of a sensitive layer is lost and the durability of a recording layer is deteriorated.

[0159] A coated amount of the lower recording layer is not particularly limited but can be selected in accordance with the use thereof, desirable sensitivity and recording properties. In the case of a planographic printing plate, generally, the amount is preferably in the range of 0.5 to 5.0 g/m<sup>2</sup>, more preferably 0.5 to 1.9 g/m<sup>2</sup>.

#### [Other components]

[0160] For forming the aforementioned positive recording layers (upper recording layer, lower recording layer), in addition to the above essential components, a variety of additives can be added, if necessary, so long as the effects of the present invention are not impaired. As an example, substances exemplified in the first aspect of the present invention can be used. In addition, preferable ones are also preferable.

[0161] Each of the upper recording layer and the lower recording layer of the planographic printing plate precursor of the present invention can be manufactured by coating a solution for the lower recording layer on a suitable support and, then, coating a coating solution for the upper recording layer thereon. In addition, two or more recording layers may be coated together by using a prescribed apparatus (overlap-coating two recording layers).

[0162] As a solvent used for coating, the solvents used for dissolving components in order to form the recording layer in the first aspect are also exemplified and used for the second aspect. Preferable examples of the first aspect are also preferable, but it is not limited thereto.

[0163] When the upper recording layer and the lower recording layer are provided adjacent to each other, it is preferable that a solvent of the coating solution for the upper recording layer, which does not substantially dissolve a lower recording layer, is selected, in order to prevent mix of the layers at an interface thereof.

[0164] The concentration of the aforementioned component (all solids including additives) in a solvent is preferably in an amount of 1 to 50% by weight.

[0165] As a coating method, a variety of methods described in the first aspect can be used. Further, preferable examples and amounts of materials described in the first aspect are also preferable.

#### [Support]

[0166] As a support used in the second aspect of the present invention, a plate having the dimensional stability, with the necessary strength and the durability is exemplified. Supports mentioned in the first aspect can be used. Preferable examples of the first aspect are also preferable.

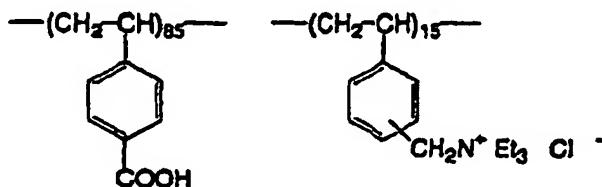
[0167] The planographic printing plate precursor of the second aspect of the present invention comprises at least two positive recording layers on a support. As necessary, a subbing layer may be provided between the support and the lower recording layer. The subbing layer described in the first aspect can be used. Preferable examples of the first

## [Preparation of a support]

[0180] An aluminum plate (material: 1050) having a thickness of 0.3 mm was degreased by washing with trichloroethylene, the surface thereof was grained using a nylon brush and a 400 mesh Parnis-water suspension, and washed well with water. This plate was immersed in a 25% aqueous sodium hydroxide solution at 45°C for 9 seconds to etch it. The plate was washed with water, and further immersed in a 20% nitric acid for 20 seconds, and washed with water. An etching amount of the grained surface was about 3 g/m<sup>2</sup>. Then, 3 g/m<sup>2</sup> direct current anodized film was provided on this plate by using 7% sulfuric acid as an electrolysis solution at the current density of 15 A/dm<sup>2</sup>. Subsequently, the plate was washed with water, dried, further treated with an aqueous solution of 2.5% by weight of sodium silicate at 30°C for 10 seconds. And then, following subbing solution was coated on the plate, and the formed film was dried at 80°C for 15 seconds to obtain a support. An amount of the formed film after drying was 15 mg/m<sup>2</sup>.

## [Subbing solution]

The following compound	0.3g
Methanol	100g
Water	1g



Molecular weight 2,8000

## (Example 1)

[0181] The support was coated with a following sensitizing solution 1 at a coated amount of 1.0 g/m<sup>2</sup>, and dried at 140°C for 50 seconds to obtain a planographic printing plate precursor 1. "PERFECT OVEN PH200" manufactured by TABAI was used for the drying and a Wind Control thereof is set to 7.

## [Sensitizing solution 1]

Ammonium salt (1)	0.04g
m,p-cresol novolac (m/p ratio=6/4, weight average molecular weight 3500, containing 0.5% by weight of unreacted cresol)	0.474g
A specific copolymer 1 described in JP-A No. 11-288093	2.37g
Cyanine dye A (having a structure below)	0.155g
2-methoxy-4-(N-phenylamino)benzene diazonium hexafluorophosphate	0.03g
Tetrahydrophthalic anhydride	0.19g
Ethyl violet in which a counterion thereof is changed to 6-hydroxy-β-naphthalenesulfonic acid	0.05g
Fluorine containing surfactant (Megafac F 176PF, manufactured by Dainihoninki Kagaku Kogyo K.K.)	0.035g
Fluorine containing surfactant (Megafac MCF-312, manufactured by Dainihoninki Kagaku Kogyo K.K.)	0.05g
Paratoluene sulfonic acid	0.008g
Bis-p-hydroxyphenylsulfone	0.063g
Dodecyl stearate	0.06g

(continued)

[Sensitizing solution 3-A]		
5	2-methoxy-4-(N-phenylamino)benzene diazonium hexafluorophosphate	0.01g
	Tetrahydrophthalic anhydride	0.19g
	Ethyl violet in which a counter ion thereof is changed to 6-hydroxy- $\beta$ -naphthalenesulfonic acid	0.05g
	Fluorine containing surfactant (Megafac F 176PF, manufactured by Dainihoninki Kagaku Kogyo K.K.)	0.035g
	Fluorine containing surfactant (Megafac MCF-312, manufactured by Dainihoninki Kagaku Kogyo K.K.)	0.05g
10	p-toluenesulfonic acid	0.008g
	Bis-p-hydroxyphenylsulfone	0.06g
	$\gamma$ -butyrolactone	13g
	Methyl ethyl ketone	24g
15	1-methoxy-2-propanol	11g

[Sensitizing solution 3-B]		
20	Ammonium salt (1)	0.1g
	m,p-cresol novolac (m/p ratio=6/4, weight average molecular weight 5000, containing 0.5% by weight of unreacted cresol)	0.237g
	Cyanine dye A	0.025g
	2-methoxy-4-(N-phenylamino)benzene diazonium hexafluorophosphate	0.01g
25	Fluorine containing surfactant (Megafac F 176PF, manufactured by Dainihoninki Kagaku Kogyo K.K.)	0.035g
	Fluorine containing surfactant (Megafac MCF-312, manufactured by Dainihoninki Kagaku Kogyo K.K.)	0.05g
	Bis-p-hydroxyphenylsulfone	0.003g
	Dodecyl stearate	0.03g
	Methyl ethyl ketone	15g
30	1-methoxy-2-propanol	8g

(Example 4)

35 [0184] The support was coated with a following sensitizing solution 3-A such that a coated amount after drying is 0.85 g/m<sup>2</sup>, and dried at 140°C for 50 seconds. Subsequently, the obtained plate was coated with a sensitizing solution 4 at a coated amount after drying of 0.15 g/m<sup>2</sup>, and dried at 120°C for 60 seconds to obtain a planographic printing plate precursor 4. The PERFECT OVEN PH200 manufactured by TABAI was used for the drying and a Wind Control thereof is set to 7.

[Sensitizing Solution 4]		
40	Ammonium salt (1) m,p-cresol novolac (m/p ratio=6/4, weight average molecular weight 5000, containing 0.5% by weight of unreacted cresol)	0.35g
	Cyanine dye A	0.237g
45	2-methoxy-4-(N-phenylamino)benzene diazonium hexafluorophosphate	0.01g
	Fluorine containing surfactant (Megafac F 176PF, manufactured by Dainihoninki Kagaku Kogyo K.K.)	0.035g
	Fluorine containing surfactant (Megafac MCF-312, manufactured by Dainihoninki Kagaku Kogyo K.K.)	0.05g
	Bis-p-hydroxyphenylsulfone	0.003g
50	Dodecyl stearate	0.03g
	Methyl ethyl ketone	15g
	1-methoxy-2-propanol	8g

(Example 5)

55 [0185] The support was coated with a following sensitizing solution 3-A such that a coated amount after drying is 0.85 g/m<sup>2</sup>, and dried at 140°C for 50 seconds. Subsequently, the plate was coated with a sensitizing solution 5 at a coated amount after drying of 0.15 g/m<sup>2</sup>, and dried at 120°C for 60 seconds to obtain a planographic printing plate

## (Comparative Example 2)

[0189] A planographic printing plate precursor 19 was prepared in the same manner as Example 2, except that the ammonium salt (1) was not added in the sensitizing solution 2 of Example 2.

## (Comparative Example 3)

[0190] A planographic printing plate precursor 20 was prepared in the same manner as Example 3, except that the ammonium salt (1) was not added in the sensitizing solution 3-B in Example 3.

## [Evaluation of a planographic printing plate precursor]

## [Scratch resistance test (1)]

[0191] The resulting planographic printing plate precursors 1 to 14 of the present invention and planographic printing plate precursors 15 to 17 of Comparative Examples were rubbed 30 times with an abraser felt CS 5 under 250g load using a rotary abrasion tester manufactured by TOYOSEIKI.

[0192] Thereafter, a developing solution DT-1 or DP-4 manufactured by Fuji Film Co., Ltd. (diluted 1:8 with tap water) was placed in a PS processor 900H manufactured by Fuji Film Co., Ltd., and developments of the precursors were performed at a temperature of 30°C for a development time of 12 seconds. As a gum solution, FP-2W (diluted 1:1 with tap water) was used.

[0193] A developing solution DT-1 is a so-called non-silicate developing solution, and DP-4 is a silicate-containing developing solution.

[0194] Evaluation of the scratch (blotch or scar) resistance property was performed under the following criteria. The results are shown in Table 3 below. Usually, no problem on the scratch resistance property (scratch resistance ability) under the criteria satisfies the practical performance.

O: The optical density of a rubbed portion of a photosensitive film was not changed as compared with those of a non-rubbed portion.

X: The optical density of a rubbed portion of a photosensitive film was considerably reduced as compared with those of a non-rubbed portion.

## [Scratch resistance test (2)]

[0195] A scratching scratch was provided on the planographic printing plate precursors with a successively loading-type scratching strength tester TYPE-HEIDON-18 (manufactured by Shinto Kagaku K.K.) wherein a diamond needle (R=0.4 mm) is utilized, scratching rate is 50 mm/sec and a load applied was varied.

[0196] Thereafter, a developing solution DT-1 or DP-4 manufactured by Fuji Film Co., Ltd. (diluted 1:8 with tap water) was placed in a PS processor 900H manufactured by Fuji Film Co., Ltd., and development of the precursors was performed at a solution temperature of 30°C and a developing time of 12 seconds. As a gum solution, FP-2W (diluted 1:1 with tap water) was used. The plate after development was evaluated with naked eyes, and a maximum load (g) giving no scratch was adopted as the scratching scratch strength. The results are shown in Table 3 below.

[0197] Usually, the maximum load of 5g or greater is a level of no practical problem and the maximum load of 10g or greater is extremely excellent in the scratch resistance property. A plate having the maximum load can stand the excess severe handling.

## [Development Latitude Evaluation (1)]

[0198] A test pattern image was formed on the resulting planographic printing plate precursors 1 to 17 of the present invention and the planographic printing plate precursors 18 to 20 of Comparative Examples with an infrared laser at the beam strength of 9w and a drum rotating rate of 150 rpm with a Trendsetter manufactured by Creo Products Inc.

[0199] Thereafter, a developing solution DT-1 or DT-4 manufactured by Fuji Film Co., Ltd. (diluted 1:8 with tap water) was placed in a PS processor 900H manufactured by Fuji Film Co., Ltd., and development was performed at a solution temperature of 30°C and a development time of 12 seconds. As a gum solution, FP-2W (diluted 1:1 with tap water) is used. All planographic plates obtained under this condition show excellent developability at an exposed portion.

[0200] Next, assuming a condition under which a developer was concentrated, above developing solution was changed to a developing solution which was prepared by diluting in a dilution ratio of 1:7 with tap water. An exposed planographic printing plate was developed similarly at a solution temperature of 30°C and a development time of 12

Table 3 (continued)

		Developing solution	Scratch resistance test (1)	Scratch resistance test (2)	Evaluation of development latitude (1)
Example 11	Planographic printing plate precursor 11	DT-1	O	15g	O
Example 12	Planographic printing plate precursor 12	DT-1	O	5g	O
Example 13	Planographic printing plate precursor 13	DT-1	O	5g	O
Example 14	Planographic printing plate precursor 14	DT-1	O	5g	O
Example 15	Planographic printing plate precursor 15	DT-1	O	5g	O
Example 16	Planographic printing plate precursor 16	DT-1	O	5g	O
Example 17	Planographic printing plate precursor 17	DT-1	O	5g	O
Comparative Example 1	Planographic printing plate precursor 18	DP-4	x	less than 5g	x
Comparative Example 2	Planographic printing plate precursor 19	DT-1	x	less than 5g	x
Comparative Example 3	Planographic printing plate precursor 20	DT-1	x	less than 5g	x

[0203] As shown in Table 3, the planographic printing plate precursors of the present invention are excellent in the scratch resistance property as compared with those of Comparative Examples. Further, in the planographic printing plate precursors of the present invention, the decrease of the density of an image portion was not observed even when the developing solution of high concentration was used and, thus, the excellent development latitude is obtained.

[Evaluation of development latitude (2)]

[0204] Assuming a condition under which a developing solution is more concentrated, the similar evaluation was carried out.

[0205] A test pattern image was formed on the planographic printing plate precursors 1 to 14 of the present invention and the planographic printing plate precursors 15 to 17 of Comparative Examples with an infrared laser at the beam strength 9w and a drum rotating rate of 150 rpm with Trendsetter manufactured by Creo Products Inc.

[0206] Next, a developing solution DT-1 or DP-4 manufactured by Fuji Film Co., Ltd. (diluted 1:6 with tap water) was placed in a PS processor 900H manufactured by Fuji Film Co., Ltd., and development was performed at a solution temperature of 30°C and a development time of 12 seconds.

[0207] As described above, the decrease in the optical density at an unexposed portion of the recording layer in the planographic printing plate after development was evaluated with naked eyes, and the image formation property when

Table 4 (continued)

		Developing solution	Evaluation of development latitude (2)	Evaluation of development latitude (1)
5	Example 11	DT-1	O	O
10	Example 12	DT-1	Δ	O
15	Example 13	DT-1	Δ	O
20	Example 14	DT-1	Δ	O
25	Example 15	DT-1	Δ	O
30	Example 16	DT-1	Δ	O
35	Example 17	DT-1	Δ	O
40	Comparative Example 1	DP-4	x	x
	Comparative Example 2	DT-1	x	x
	Comparative Example 3	DT-1	x	x

[0209] As apparent from Table 4 and the Table 3, the planographic printing plate precursor of the present invention has the remarkable effect in both scratch resistance property and development latitude, particularly when a non-silicate developing solution was used for development. In addition, among the precursors, a planographic printing plate precursor comprising a recording layer which contains an organic quaternary ammonium salt having an aryl group or a carbonyl group and a planographic printing plate precursor having a recording layer of the multilayer structure and an upper layer thereof were found to provide excellent effects.

[0210] According to the first aspect of the present invention, there can be provided an positive planographic printing plate precursor for use with an infrared laser which is used for a direct plate and which has an excellent latitude at the time of development for forming an image and has the excellent scratch resistance property.

[0211] The second aspect of the present invention will be explained by referring Examples below, but the scope of the present invention is not limited to the Examples.

[Preparation of a support]

[0212] A support was prepared in a same way as Examples of the first aspect.



Table 5

	Planographic printing plate precursor	Coated amount (g/m <sup>2</sup> )		Infrared absorbent		Load at parallelable scratch (g)	Sensitivity (mJ/cm <sup>2</sup> )	Electric conductivity of developing solution for image forming (mS/cm)	Resistance to chemicals (×10,000)
		Upper recording layer	lower recording layer	Upper recording layer	lower recording layer				
Example 18	21	0.27	0.85	Presence	Presence	75	67	43-51	30
Example 19	22	0.08	1.10	Presence	Presence	50	42	41-49	35
Example 20	23	0.40	0.65	Presence	Presence	120	75	45-55	25
Comparative Example 4	24	0.55	0.83	Presence	Presence	135	130	52-75	5
Comparative Example 5	25	0.28	0.83	Absence	Presence	80	100	57-75	8
Comparative Example 6	26	0.28	0.80	Presence	Absence	3	67	43-45	6

an excellent development latitude and excellent chemical resistance.

[0225] On the other hand, the planographic printing plate precursor of Comparative Example 4 in which an upper recording layer is too thick and the planographic printing plate precursor of the Comparative Example 5 in which an upper recording layer does not contain an infrared-absorbing dye have poor sensitivity. Further, the planographic printing plate precursor of Comparative Example 6 in which a lower recording layer does not contain an infrared-absorbing dye easily damaged by scratch, has the narrow development latitude and, thus, it is not suitable for practical use.

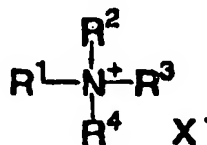
[0226] As described above, since the planographic printing plate precursor of the second aspect of the present invention is excellent in the sensitivity at image formation and development latitude, excellent image can be formed effectively at the low energy, defects resulting from a scratch at an image portion can be inhibited. Further, since a printed image obtained from planographic printing plate is hardly influenced by fine scratches on the surface of the plate, the handling properties are better. Furthermore, vain steps such as reexposure of a plate can be omitted, and it is suitable for practical use.

[0227] According to the second aspect of the present invention, there can be obtained a positive planographic printing plate precursor for use with an infrared laser for direct plate making, wherein a recording layer thereof have an excellent sensitivity and development latitude when an image is formed, and the recording layer can suppress an occurrence of defects resulting from a scratch of an image portion, and which can form the better image.

#### Claims

1. A positive planographic printing plate precursor, comprising a support having disposed thereon a positive recording layer containing (A) a water-insoluble and alkali-soluble resin, (B) an infrared absorbent and (C) an organic quaternary ammonium salt, wherein solubility of the recording layer in an aqueous alkali solution is increased by exposure to an infrared laser.
2. The positive planographic printing plate precursor according to claim 1, wherein the (C) organic quaternary ammonium salt has in a molecule thereof at least one of an aryl group and a carbonyl group.
3. The positive planographic printing plate precursor according to claim 1, wherein the (C) organic quaternary ammonium salt has in a molecule thereof both an aryl group and a carbonyl group.
4. The positive planographic printing plate precursor according to claim 1, wherein the (C) organic quaternary ammonium salt is represented by the following general formula (I):

#### General formula (I)



wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are each independently an organic group having one or more carbon atoms, and they may be bonded with each other to form a ring.

5. The positive planographic printing plate precursor according to claim 4, wherein at least one of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is selected from the group consisting of the following structures:

(19)



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(54) **Planographic printing plate precursor**

(57) A positive planographic printing plate precursor comprising a recording layer containing a water-insoluble and alkali-soluble resin, an infrared absorbent and an organic quaternary ammonium salt. A positive planographic printing plate precursor comprising at least

two recording layers containing the resin and the infrared absorbent with a coating amount of an upper positive recording layer being in the range of 0.05 to 0.45 g/m<sup>2</sup>.

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**CLAIMS INCURRING FEES**

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

**LACK OF UNITY OF INVENTION**

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 12 8353

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
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